

# UNCLASSIFIED

AD NUMBER
AD434730
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAR 1964. Other requests shall be referred to Office of Naval Research, Arlington, VA 22203.
AUTHORITY
ONR ltr dtd 28 Jul 1977

THIS PAGE IS UNCLASSIFIED

**UNCLASSIFIED**

**AD 434730**

**DEFENSE DOCUMENTATION CENTER**

**FOR**

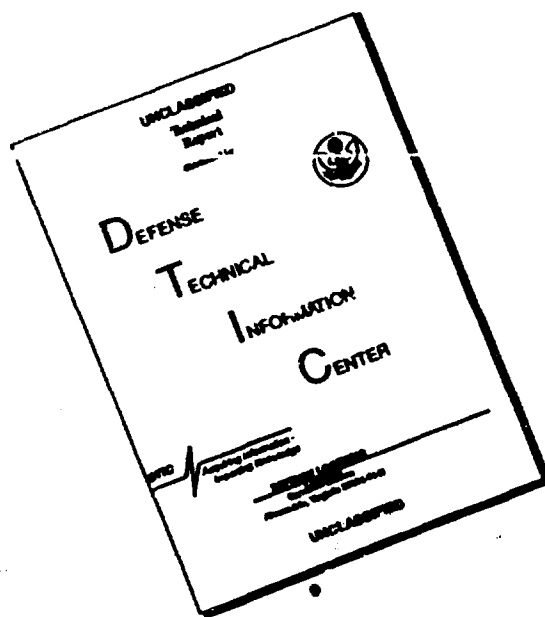
**SCIENTIFIC AND TECHNICAL INFORMATION**

**CAMERON STATION, ALEXANDRIA, VIRGINIA**



**UNCLASSIFIED**

# DISCLAIMER NOTICE



**THIS DOCUMENT IS BEST  
QUALITY AVAILABLE. THE COPY  
FURNISHED TO DTIC CONTAINED  
A SIGNIFICANT NUMBER OF  
PAGES WHICH DO NOT  
REPRODUCE LEGIBLY.**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CATALOGED BY DUU

434730

AS AD No. \_\_\_\_\_

NO OTS



THE KINETIC EQUATION  
OF CLASSICAL BOLTZMANN GASES

C. H. Su

Department of Mechanical Engineering  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
Cambridge, Massachusetts

Acknowledgments.

This work has been sponsored by the Advanced Research Projects Agency (Ballistic Missile Defense Office) and technically administered by the Fluid Dynamics Branch of the Office of Naval Research under Contract Nonr-1841(93).

It is a great pleasure to acknowledge discussions with E. A. Frieman, M. D. Kruskal, and Dr. R. Goldman of the Princeton Plasma Physics Laboratory.

Thanks also go to R. F. Probstein and J. E. McCune of M. I. T. for their interests in the problem and the careful reading of the manuscript.

Abstract.

By use of the multiple-time-scale method, the low density expansion is carried to the order of the triple collision integral. The validity of Bogoliubov's assumption that the multiple distribution depends functionally on a single particle distribution is carefully examined. It is found that such an assumption is valid except locally for those particles which have a large separation at a time  $t$  and which have their relative velocity so oriented that they were in collision at  $t = 0$ . Since this local breakdown is very selective, the triple collision integral which is found in the literature is still correct. As a by-product of the multiple-time-scale method, the rate at which a system approaches the kinetic state is obtained; it is also found that up to the order we have considered the Maxwellian distribution is the only solution at thermal equilibrium.



## I. Introduction.

During the past decade, various methods have been developed for the derivation of the Boltzmann collision integral from first principles of mechanics (Bogoliubov,<sup>1</sup> Prigogine and his co-workers,<sup>2</sup> Green,<sup>3</sup> and Kirkwood and his co-workers<sup>4</sup>). Recently the correction to the Boltzmann (binary) collision integral has also been obtained by various investigators (Choh and Uhlenbeck,<sup>5</sup> M. Green,<sup>6</sup> Rice, Kirkwood and Harris,<sup>7</sup> and Resibois<sup>8</sup>). The relationship of various methods was first discussed by Cohen<sup>9,10</sup> who established within certain assumptions the equivalence of the method of Bogoliubov and Green. More recently Sandri<sup>11</sup> and McCune, Sandri and Frieman<sup>12</sup> studied the problem of the low density expansion of the B-B-G-K-Y hierarchy by the method of multiple-time-scales. They found that the triple collision integral obtained by the previous investigators is divergent. The physical nature of this divergence was not studied in any detail. On the other hand, the nature of the higher order corrections to the Fokker-Planck collision integral was carried out in great detail by Su.<sup>13</sup> The nature of local singularities in the solution for correlation function was displaced there. Well-behaved correction terms to the Fokker-Planck collision integral were obtained.

In this paper, we shall use the method of multiple-time-scales to investigate the nature of Boltzmann collision integral and its correction terms under the assumption of spatial homogeneity. This systematic expansion procedure offers a simple way to demonstrate to what extent the Bogoliubov assumption regarding the higher distribution functions as functionals of the first distribution is valid. It is found, up to the triple collision level, in contrast to the works in Refs. 11 and 12, that

Bogoliubov's assumption is valid except for a special local region in two-particle phase space, i.e., for two particles having a large separation at time  $t$  and with their relative velocity oriented in such a way (say in reference to their relative position vector) that they were in collision at  $t = 0$ . This same local breakdown was first found in the investigation of a weak coupling gas<sup>13</sup> which leads to Fokker-Planck equation in its lowest order approximation.

Cohen,<sup>14</sup> in his investigation of the triple collision, also found it necessary to neglect the kind of singularity mentioned above in order that the equation for the first order two-particle function would admit any solution at all. He remarked that, for the "large majority" of cases, the equation for the two-particle function due to the triple interaction was solvable and has a well-behaved solution. He seemed also to encounter the same difficulty in Ref. 10 where he suggested a coarse-graining procedure.

We shall indeed see that the secularity we have found can be eliminated by an averaging process in the momentum space, provided we restrict ourselves to the triple collision level. As one goes to higher orders such an averaging is no longer sufficient to smooth out the local singularity.

It is suggested by the nature of the singularity, that a new scaling be applied to the hierarchy equation in this special region in phase space. The unit of time and length in this region is taken to be the mean free time and mean free path respectively in contrast to the duration of collision and range of interaction outside the special region. There is no longer a separation of time scales in this region. The hierarchy

equations have to be solved jointly on one time scale (kinetic time scale). However, we note that the one-particle function is affected by the two-particle function only "grossly," i.e., through the following integral operator:

$$\int \underline{dx} \, dv_2 \, \frac{d\phi}{dx} \cdot \frac{\partial}{\partial v_1}$$

Here  $\underline{x}$  is the relative position between particles 1 and 2, and  $\phi$  is the interparticle potential. The subscript 1 (or 2) refers to the particle 1 or 2. The velocity integration above provides the coarse-graining process which we mentioned earlier; this is, however, not sufficient at higher orders because the singularity in the two-particle function then becomes too strong. Since in the special region, the separation of the two particles has to be large, if the range of the pair potential is very limited, the contribution of any singularity at large  $\underline{x}$  will be strongly de-emphasized by the potential force  $d\phi/d\underline{x}$  under the integral sign. We therefore conclude that even though Bogoliubov's assumption becomes locally invalid in a local region, the triple collision integral obtained in the literature is correct. The procedure of solving the hierarchy equations, such as that given by Choh and Uhlenbeck,<sup>5</sup> can apparently be pushed to higher order, provided the pair potential between the particles is sufficiently short-ranged.

We shall formulate our problem as an initial value problem. Since the relevant correlations between particles are those created through the interaction of particles, the initial values for all correlation functions will be taken to be zero. The effects of the initial values of correlation functions on the one-particle kinetic equation were studied

in Ref. 13. Within the framework of the multiple-time-scale formulation, all the physical changes in the problem appear in their own appropriate time scales automatically: relaxation towards the kinetic stage on the fast time scale (of the order of the collision time), kinetic evolution on the slow time scale (of the order of the mean free time). For the spatially homogeneous system which we shall analyze, the time scales end automatically at the kinetic time scale, which, of course, is what one would expect physically.

## II. Binary Collision Integral.

The first three members of the B-B-G-K-Y hierarchy for a spatially homogeneous system under the low density approximation are as follows:

$$\frac{\partial f}{\partial t} = \epsilon \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial g}{\partial \underline{v}_1} \quad , \quad (1)$$

$$\frac{\partial g}{\partial t} + \underline{v}_{12} \cdot \frac{\partial g}{\partial \underline{x}} - \frac{1}{m} \frac{\partial \phi}{\partial \underline{x}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2} \right) [g(\underline{x}) + f(1)f(2)] \quad (2)$$

$$= \epsilon \frac{n}{m} \int d\underline{\xi} d\underline{v}_3 \frac{d\phi}{d\underline{\xi}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} [f(1)g(\underline{\xi}-\underline{x}, 23) + h(\underline{x}, \underline{\xi}, 123)] \right. \\ \left. - \frac{\partial}{\partial \underline{v}_2} [f(2)g(\underline{x}-\underline{\xi}, 13) + h(\underline{x}, \underline{x}-\underline{\xi}, 123)] \right) \quad ,$$

$$\frac{\partial h}{\partial t} + \underline{v}_{12} \cdot \frac{\partial h}{\partial \underline{x}} + \underline{v}_{13} \cdot \frac{\partial h}{\partial \underline{\xi}} - \frac{1}{m} \frac{\partial \phi}{\partial \underline{x}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2} \right) [h + f(1)g(23) + f(2)f(13)] \\ - \frac{1}{m} \frac{\partial \phi}{\partial \underline{\xi}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_3} \right) [h + f(1)f(23) + f(3)f(12)] \\ - \frac{1}{m} \frac{\partial \phi(\underline{x}-\underline{\xi})}{\partial \underline{\xi}} \cdot \left( \frac{\partial}{\partial \underline{v}_2} - \frac{\partial}{\partial \underline{v}_3} \right) [h + f(2)f(13) + f(3)g(12)] \\ = \text{integral term with the leading term of order } \epsilon. \quad (3)$$

Here  $f$  is the one-particle distribution function;  $g$  and  $h$  are the two- and three-particle correlation functions which are related to the two- and three-particle distribution functions as follows:

$$f(1) = F_1(1)$$

$$g(12) = F_2(2) - f(1)f(2)$$

$$h(123) = F_3(123) - f(1)g(12) - f(2)g(13) - f(3)g(12)$$

The time variable in the above functions is omitted for simplicity. The numbers within each bracket indicate the specific particles in which we are interested.

$\underline{x}$  and  $\underline{r}$  are the position vectors of particle 1 relative to particles 2 and 3 respectively. The small parameter  $\epsilon$  equals the average number of particles within the range of the pair potential which is assumed to be repulsive and finite in range.

The time and length in Eqs. (1) to (3) have been normalized by the duration of a collision and the range of the pair potential respectively. The mean free path of close collisions, in which we are interested, can be given as follows:

$$l = \frac{1}{nr_0^2}$$

where  $n$  is the average density and  $r_0$  is the radius of the collision cross-section. Identifying the latter as the range of the pair potential, we see that the ratio of the range of potential to the mean free path (or the ratio of the collision time to the mean free time) is  $\epsilon$ . For very small  $\epsilon$ , we have therefore two distinct time scales in our problem: a

fast time which is of the order of the collision time and a slow time which is of the order of the mean free time. In the method of multiple-time-scale, the slow time, as well as the fast time, is treated as independent variables, i.e., we extend  $f(t)$  to  $f(t, \epsilon t, \epsilon^2 t, \dots)$ .<sup>\*</sup> The extra freedom introduced is used to demand that the solution for  $f$  be well-behaved in the limit of  $t \rightarrow \infty$ , i.e., no secular behavior for  $g(t \rightarrow \infty)$ . Formally this extension in the time variable is equivalent to the expansion of the time derivative in the following way:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial t_0} + \epsilon \frac{\partial}{\partial t_1} + \epsilon^2 \frac{\partial}{\partial t_2} + \dots, \quad (4)$$

where

$$\frac{dt_0}{dt} = 1, \quad \frac{dt_1}{dt} = \epsilon, \quad \text{and so on.}$$

We now expand  $f$ ,  $g$ , and  $h$  in simple power series in  $\epsilon$ , for example,

$$f = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \dots \quad (5)$$

From the zero order equations of  $f$ , it is seen that  $f^{(0)}$  is  $t_0$  independent. The equation for  $g^{(0)}(\underline{x}, 12, t_0)$  is

$$\frac{\partial f^{(0)}}{\partial t_0} + \underline{v}_{12} \frac{\partial f^{(0)}}{\partial \underline{x}} - \frac{1}{m} \frac{\partial \phi}{\partial \underline{x}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2} \right) f^{(0)} = \frac{1}{m} \frac{\partial \phi}{\partial \underline{x}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2} \right) f^{(0)}(1) f^{(0)}(2) \quad (6)$$

Its solution is easily found (since  $f^{(0)}$  is  $t_0$  independent) as

$$f^{(0)}(\underline{x}, 12, t_0) = [S_{-t_0}(12) - 1] f^{(0)}(1) f^{(0)}(2) \quad (7)$$

---

<sup>\*</sup> The inclusion of  $\epsilon^2 t$  and so forth is purely a mathematical procedure. A discussion of the termination of time scales is given at the end of the next section.

where  $S_{-t_0}(12) = \exp[-t_0 H(12)]$  is the two-particle streaming operator and

$$H(12) = v_{12} \cdot \frac{\partial}{\partial \underline{x}} - \frac{1}{m} \frac{\partial \phi}{\partial \underline{x}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2} \right)$$

The one particle function up to this order of approximation is

$$\frac{\partial f^{(1)}}{\partial t_0} + \frac{\partial f^{(0)}}{\partial t_1} = \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial f^{(0)}(\underline{x}, 12, t_0, t_1)}{\partial \underline{v}_1} \quad (8)$$

If we integrate this equation in  $t_0$ , the second term on the left side of Eq. (8) will be proportional to  $t_0$ . To avoid the secularity due to  $\partial f^{(0)}/\partial t_1$  in the solution for  $f^{(1)}$  on the time scale  $t_0$ , we require

$$\frac{\partial f^{(0)}}{\partial t_1} = \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial}{\partial \underline{v}_1} [S_{-\infty}(12) f^{(0)}(1) f^{(0)}(2)] \quad (9)$$

and

$$\frac{\partial f^{(1)}}{\partial t_0} = \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial}{\partial \underline{v}_1} [S_{-t_0}(12) - S_{-\infty}(12)] f^{(0)}(1) f^{(0)}(2) \quad (10)$$

The integral term in (9) can be transformed into the usual Boltzmann collision integral (binary). It is seen from Eq. (9) that the kinetic evolution is in a time scale of order  $1/\epsilon$  compared with the duration of a collision. It was shown that the former is just the mean time between collisions.

Equation (10) gives the transient towards the kinetic stage governed by Eq. (9). The  $(t_0)$  time behavior of the source function on the right side of Eq. (10) can be analyzed as follows. The pair potential has been assumed to have a finite range. At time  $t_0$ , because of the factor  $d\phi/d\underline{x}$  in Eq. (10), the particle 2 must be within the range of particle

1 in order that the integral be different from zero. For sufficiently large  $t_0$ ,  $S_{-t_0}(12)$  will definitely bring particle 2 outside the range of particle 1.\* If the pair potential has an exponential-like tail, the source function of Eq. (10) will decay exponentially in  $t_0$  as  $t_0$  tends to infinity. Therefore, in that case, the approach to the kinetic stage is exponentially fast in the time scale of the collision time.

### III. Triple Collision Integral.

The zero order three-particle correlation function can be obtained from (3) as

$$\begin{aligned} h^{(0)}(\underline{x}, \underline{\xi}, 123, t_0) = & [S_{-t_0}(123) - 1] \\ & - [S_{-t_0}(12) - 1] \\ & - [S_{-t_0}(23) - 1] \\ & - [S_{-t_0}(31) - 1] \} f^{(0)}(1)f^{(0)}(2)f^{(0)}(3) \end{aligned} \quad (11)$$

where  $S_{-t_0}(123)$  is the three-particle streaming operator,  $\exp[-t_0 H(123)]$ , and  $H(123)$  is the three-particle Hamilton operator:

$$\begin{aligned} H(123) = & \underline{v}_{12} \cdot \frac{\partial}{\partial \underline{x}} + \underline{v}_{13} \cdot \frac{\partial}{\partial \underline{\xi}} - \frac{1}{m} \frac{\partial \phi}{\partial \underline{x}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2} \right) - \frac{1}{m} \frac{\partial \phi}{\partial \underline{\xi}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_3} \right) \\ & - \frac{1}{m} \frac{\partial \phi(\underline{x} - \underline{\xi})}{\partial \underline{\xi}} \cdot \left( \frac{\partial}{\partial \underline{v}_2} - \frac{\partial}{\partial \underline{v}_3} \right) \end{aligned}$$

---

\* The pair potential had been assumed to be repulsive.



The integrand of this integral in the limit of  $t_0 \rightarrow \infty$  is plotted in Fig. 1. The integral on the second line of (13) is given by the shaded area in the graph. If  $\underline{x}$  is finite, the collision of particles 1 and 2 (if they happen to collide)\* will occur at a finite  $\tau$  for any nonvanishing  $\underline{v}_{12}$ . The above mentioned area is therefore finite and hence is the integral. However if we let

$$\underline{x} = \left[ \frac{1}{\alpha} \underline{v}_{12} t_0 + \underline{y} \right] \rightarrow \infty \quad , \quad (14)$$

the integral becomes singly infinite, where  $\alpha$ ,  $\underline{y}$  are constants with  $\alpha > 1$  and  $\underline{y}$  related to the range of the pair potential. Eq. (14) indicates a very careful selection of the points in the phase space of the two interacting particles. We want the particles to have a large separation at time  $t_0$  and to have their relative velocity oriented in such a way (in reference to the direction of their relative position vector, say), that they were in collision at  $t_0 = 0$ . Such secularity was also found in the weak coupling expansion.<sup>13</sup> Mathematically it is clear that the secularity is due to the infinite range of  $f^{(0)}(12)$  in the special region of phase space mentioned above. We observe that the solution for  $g^{(0)}(12, t_0)$  given by Eq. (7) cannot be valid in this special region, since the assumption of the independence of particles 1 and 2 from the rest of the system in the lowest order approximation becomes invalid if the particles have an infinite range of correlation. The presence of a third particle cannot be ignored.

---

\* If there is no collision between the time 0 and  $t_0$ ,  $S_{-\infty} f^{(0)} f^{(0)}$  and  $S_{-1} f^{(0)} f^{(0)}$  coincide from  $\tau = 0$  and on to infinite, the integral is zero identically.

Next we consider the contribution of the integral terms to the solution for  $g^{(1)}(\underline{x}, 12, t_0)$ . Since the structure of the second square bracket of the integral term in Eq. (12) is very much the same as the first one, we shall analyze the first one only, i.e.,

$$\frac{n}{m} \int d\underline{\xi} d\underline{v}_3 \frac{d\phi}{d\underline{\xi}} \cdot \frac{\partial}{\partial \underline{v}_1} [S_{-t_0}(\underline{x}, \underline{\xi}, 123, t) - S_{-\infty}(\underline{\xi}, 13)] f^{(0)}(1) f^{(0)}(2) f^{(0)}(3) \quad (15)$$

It is seen that because of its being  $\underline{x}$  and  $t_0$  independent, the second term in the above expression will cause a secularity in the solution for  $g^{(1)}$ . To be free of secularity one usually, though not always correctly, seeks a cancellation between the first and second terms for all  $\underline{x}$  and  $\underline{\xi}$ . This led Sandri<sup>11</sup> to conclude that the cancellation is not exact for some kinds of interaction between the three particles and thus he was faced with a general secularity (non-local) in the expansion.\* However, considering the expression in Eq. (15) as a source function of the differential equation for  $g^{(1)}(\underline{x}, 12, t_0)$ , we see that the solution for  $g^{(1)}(\underline{x}, 12, t_0 \rightarrow \infty)$  depends very much on the behavior of this source function in terms of  $\underline{x}$ . It is evident that if this source function has a finite range in  $\underline{x}$ , and goes to zero sufficiently fast as  $|\underline{x}| \rightarrow \infty$ , the solution for  $g^{(1)}(\underline{x}, 12, t_0)$  will be well-behaved in the limit of  $t_0 \rightarrow \infty$ .

To investigate the variation of the source function in terms of  $\underline{x}$ , we consider that at time  $t_0$  the configuration of particles 1, 2, and 3 is as shown in Fig. 2. We assume that the three particles interact simultaneously at the time  $t_0$ . Apart from the integral operator

---

\* Sandri used the hierarchy equations for S-particle functions; the corresponding quantity which caused the secularity is then  $\partial f_2^{(0)} / \partial t_1$ .

$$\frac{n}{m} \left[ d\xi \frac{dv_3}{d\xi} \cdot \frac{\partial}{\partial v_1} \right]$$

the first term of the source function in (15) is

$$S_{-t_0}(\underline{x}, \underline{\xi}, 123) f^{(0)}(1) f^{(0)}(2) f^{(0)}(3) = f^{(0)}(1') f^{(0)}(2') f^{(0)}(3') \quad (16)$$

where  $1'$ ,  $2'$ , and  $3'$  are the velocities of the three particles at the points  $-t_0$  backwards along the particle trajectories from the initial configuration 123. For the second term in the source function the particle 2 does not interact with either 1 or 3. The trajectories of 1 and 3 are then given by the dashed lines in Fig. 2 because of the absence of 2.

Thus

$$f^{(0)}(2) S_{-\infty}(\underline{\xi}, 13) = f^{(0)}(2) f^{(0)}(1'') f^{(0)}(3'') \quad (17)$$

The points  $1''$  and  $3''$  should be projected infinitely far back from 1 and 3. After particles 1 and 3 leave the interaction zone, there is no change in their velocity; it is immaterial exactly where  $1''$  and  $3''$  are, provided they are out of the interaction zone. For such an event, (16) and (17) are not the same in the limit of  $t_0 \rightarrow \infty$ , however their difference is finite. As  $|\underline{x}|$  increases, the effect of the particle 2 on the motion of particles 1 and 3 becomes less. For a sufficiently large  $|\underline{x}|$  we see that

$$1' \rightarrow 1''$$

$$2' \rightarrow 2''$$

$$3' \rightarrow 3''$$

and the expressions in (16) and (17) exactly cancel each other except in the following two instances:

1) Two successive binary collisions  $1 * 3$  and  $3 * 2$ .<sup>\*</sup> For any finite  $|\underline{x}|$  there is no difference from the previous simultaneous interaction  $1 * 2 * 3$ . The source function does not vanish. It can be seen that the expressions (16) and (17) do not cancel each other even in the limit of  $|\underline{x}| \rightarrow \infty$  (see Fig. 3). However in such a limit we see that  $|\underline{\xi} - \underline{x}|$  also tends to be very large. This follows because  $|\underline{\xi}|$  has to be finite because of the factor  $d\phi/d\underline{\xi}$  in the source function. It can be seen that in the limit of  $|\underline{\xi} - \underline{x}| \rightarrow \infty$  in order that the second binary collision  $3*2$  occur at all, the relative velocity between 2 and 3 must be selected very carefully. The relative velocity between 3 and 2 after  $1 * 3$  (particles 3 at  $3'_0$ ) must be oriented almost in the direction of  $\underline{\xi} - \underline{x}$ . In other words, particle 3 at  $3'_0$  must aim at particle 2 which is at a large distance away. The solid angle in the relative velocity space  $\underline{v}_{23'_0}$ , within which the second binary collision is possible, goes as  $1/|\underline{\xi} - \underline{x}|^2$  as  $|\underline{\xi} - \underline{x}| \rightarrow \infty$ . We thus conclude that although the expressions in (16) and (17) do not cancel in the limit as  $|\underline{x}| \rightarrow \infty$ , the source function itself, which contains a velocity integration  $d\underline{v}_3$ <sup>†</sup>, goes to zero in the limit as  $|\underline{x}| \rightarrow \infty$ .

2) Two successive binary collisions  $1 * 3$  and  $1 * 2$ . The situation is much the same as before. In order to have such successive binary collisions in the limit as  $|\underline{x}| \rightarrow \infty$ , we require a special orientation of the relative velocity  $\underline{v}_{12}$ . Since now there is no integration over either  $\underline{v}_1$  or  $\underline{v}_2$ , the source function for this special arrangement (or equivalently the special local region in the phase space) becomes in-

---

\* The symbol \* between two numbers indicates the interaction between the two particles designated by the corresponding number.

† Note velocity  $\underline{v}_{3'_0}$ , and  $\underline{v}_3$  are related in a definite way. The integration in  $\underline{v}_{3'_0}$  amounts to an integration in  $\underline{v}_3$ .

finite in range. The contribution to the solution for  $g^{(1)}(\underline{x}, 12, t_0 \rightarrow \infty)$  becomes secular. This local secularity is very similar to that caused by the term  $\partial g^{(0)} / \partial t$ . However these two singular terms do not in general cancel each other exactly. In order to ensure the secularity of Eq. (13), the orientation of  $\underline{v}_{12}$  is determined independently of the presence of particle 3, while in Eq. (15) there is a strong dependence on particle 3 (compare Fig. 1b and Fig. 3). We therefore conclude that the solution for  $g^{(1)}(\underline{x}, 12, t)$  is locally secular at

$$\underline{x} = \left[ \frac{1}{\epsilon} (\underline{v}_{12} + \underline{\beta}) t + \underline{\gamma} \right] \cdot \infty \quad (18)$$

This expression includes Eq. (14) as a special case.

We have indicated earlier that in this special local region,  $g^{(0)}(\underline{x}, 12)$  is non-secular but has an infinite range in  $\underline{x}$ . Now  $g^{(1)}(\underline{x}, 12)$  becomes proportional to  $t_0$  as  $t_0$  becomes large. In order to preserve the asymptotic character of our series representation of  $g$  in the limit as  $t_0 \rightarrow \infty$ , we must require

$$t \ll \frac{1}{\epsilon} \quad (19)$$

and consequently from Eq. (18) and (19)

$$|\underline{x}| \ll \frac{1}{\epsilon} \quad (20)$$

Since our time and length are normalized by the collision time and range of the pair potential respectively, the inequalities (19) and (20) indicate that the formal expansion so far carried out is at most valid only for a time duration of the order of the mean free time and a length scale of the order of the mean free path. The solution for  $g^{(0)}$  cannot be valid in this special region, since the binary interaction alone

cannot be the leading approximation. In other words, when we solve for  $g(\underline{x}, 12)$  (the correlation function of 1 and 2), the presence of a third particle can no longer be ignored.

We now introduce the following scaling for the two-particle correlation function equation:

$$\begin{aligned} t &= \frac{1}{\epsilon} t' \\ x &= \frac{1}{\epsilon} x' \end{aligned} \quad (21)$$

where  $t'$  and  $x'$  will be of order unity for a time of the order of the mean free time and a particle separation of the order of the mean free path. Using Eq. (21) in Eq. (2), we obtain

$$\begin{aligned} \frac{\partial g}{\partial t'} + \underline{v}_{12} \cdot \frac{\partial g}{\partial \underline{x}'} - \frac{1}{m} \frac{\partial \phi}{\partial \underline{x}'} \cdot \left( \frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2} \right) [g(12) + f(1)f(2)] \\ = \frac{n}{m} \int d\underline{\xi} d\underline{v}_3 \frac{d\phi}{d\underline{\xi}} \cdot \left( \frac{\partial}{\partial \underline{v}_1} [f(1)g(\underline{\xi}-\underline{x}', 23) + h(\underline{x}', \underline{\xi}, 123)] \right. \\ \left. - \frac{\partial}{\partial \underline{v}_2} [f(2)g(\underline{x}'-\underline{\xi}, 13) + h(\underline{x}', \underline{x}'-\underline{\xi}, 123)] \right) \end{aligned} \quad (22)$$

This equation cannot be solved independently of  $f$  as before, since both  $f$  and  $g$  are now  $t'$  dependent. We see that the governing system in this local region is non-Markoffian and Bogoliubov's functional assumption is not valid. In other words, the evolution of the system in this local region cannot be described by a self-contained one-particle equation; the correlation functions vary in the slow time scale on their own right (not as functional of the one-particle function).

However, the contribution of such a local nonMarkoffian solution to the one-particle function is only a higher order effect because of

the velocity integration  $dv_2$  and the potential factor  $d\phi/dx$  in the one-particle equation, i.e.,

$$\frac{\partial f}{\partial t} = \frac{n}{m} \int dx dv_2 \frac{d\phi}{dx} \cdot \frac{\partial g}{\partial v_1} \quad (23)$$

For a pair potential having a range much smaller than the mean free path, the contribution of  $g$  to  $f$  from the above mentioned local region is negligibly small. We therefore conclude that as far as the one-particle function is concerned, one can ignore completely the local non-Markoffian region indicated earlier. In other words, for the correction term of the Boltzmann collision integral, one simply solves Eq. (12) for  $g^{(1)}(t \rightarrow \infty)$  and substitutes it into Eq. (23).

The solution for  $g^{(1)}(\underline{x}, 12, t_0)$  is obtained from Eq. (12) as follows:

$$\begin{aligned} g^{(1)}(\underline{x}, 12, t_0) &+ f^{(1)}(1, t_0) f^{(0)}(2) + f^{(1)}(2, t_0) f^{(0)}(1) \\ &= S_{-t_0}^{(12)} [f^{(1)}(1, t_0=0, t_1) f^{(0)}(2, t_1) \\ &+ f^{(1)}(2, t_0=0, t_1) f^{(0)}(1, t_1)] \\ &+ \frac{n}{m} \int_0^{t_0} d\tau S_{-\tau}^{(12)} \int d\underline{x} dv_3 \frac{d\phi}{dx} \cdot \left\{ \frac{\partial}{\partial v_1} S_{-t_0+\tau}(\underline{x}, \underline{x}, 123) \right. \\ &- S_{-t_0+\tau}^{(12)} \frac{\partial}{\partial v_1} S_{-\tau}(\underline{x}, 13) - \frac{\partial}{\partial v_2} S_{-t_0+\tau}(\underline{x}, \underline{x}-\underline{x}, 123) \\ &+ S_{-t_0+\tau}^{(12)} \frac{\partial}{\partial v_2} S_{-\tau}(-\underline{x}, 23) \left. \right\} f^{(0)}(1) f^{(0)}(2) f^{(0)}(3) \end{aligned} \quad (24)$$

where  $f^{(1)}(t_0=0)$  is the initial value of  $f^{(1)}(t_0)$ .

For the investigation of the one-particle equation, the second and

third terms on the left side of Eq. (24) can be ignored because of the  $\underline{x}$  integration in Eq. (23). Given a finite  $\underline{x}$ , for sufficiently large  $t_0$ , the variation in  $\tau$  of the first two terms inside the curly brackets of Eq. (24) is as shown in Fig. 4. The little bump near  $\tau = t_0$  represents the interaction of the particles at the time  $t_0$ . Note that the successive binary collisions discussed earlier have been neglected. In other words, the local region as indicated in Eq. (18) is excluded in the present discussion.

The operator  $S_{-\tau}^{(12)}$  makes the contribution of a function which has a finite range in  $|\underline{x}|$ , completely negligible in the limit of large  $\underline{x}$ . Therefore as far as the integral over  $\tau$  in Eq. (24) is concerned, we can neglect the bump in Fig. 4 and the corresponding expression for Eq. (24) is

$$\begin{aligned} F_2^{(1)}(\underline{x}, 12, t_0 \rightarrow \infty, t_0) &= g^{(1)}(12) + f^{(1)}(1)f^{(0)}(2) + f^{(1)}(2)f^{(0)}(1) \\ &= S_{-\infty}^{(12)} [f^{(1)}(1, t_0)f^{(0)}(2, t_1) + f^{(1)}(2, t_1)f^{(0)}(1, t_1)] \\ &+ \frac{n}{m} \int_0^\infty d\tau S_{-\tau}^{(12)} \int d\underline{x} d\underline{v}_3 \frac{d\phi}{d\underline{x}} \cdot \left\{ \frac{\partial}{\partial \underline{v}_1} S_{-\infty}(\underline{x}, \underline{x}, 123) \right. \\ &- S_{-\infty}^{(12)} \frac{\partial}{\partial \underline{v}_1} S_{-\infty}(\underline{x}, 13) - \frac{\partial}{\partial \underline{v}_2} S_{-\infty}(\underline{x}, \underline{x}, 123) \\ &- S_{-\infty}^{(12)} \frac{\partial}{\partial \underline{v}_2} S_{-\infty}(\underline{x}, 23) \} f^{(0)}(1)f^{(0)}(2)f^{(0)}(3) \end{aligned} \quad (25)$$

This expression for  $F_2^{(1)}$  is equivalent to the one obtained by Choh and Uhlenbeck except for the first term on the right side, which vanishes



for  $f^{(1)}(t_0=0) = 0$ . It was first pointed out by Sandri<sup>11</sup> that the role of the functional dependence in the Bogoliubov method was played by the term  $\partial g^{(0)}/\partial t_1$  in the multiple-time-scale formulation. Still ignoring the successive binary collisions discussed earlier, the solution of Eq. (25) can be written in the following more familiar form:<sup>14</sup>

$$\begin{aligned} F_2(\underline{x}, 12, t_0 \rightarrow \infty) = & S_{-\infty}(12) [f^{(1)}(1)f^{(0)}(2) + f^{(1)}(2)f^{(0)}(1)] \\ & + \int d\underline{\xi} d\underline{v}_3 [S_{-\infty}(\underline{x}, \underline{\xi}, 123) - S_{-\infty}(\underline{x}, 12) S_{-\infty}(\underline{\xi}, 13) \\ & - S_{-\infty}(\underline{x}, 12) S_{-\infty}(\underline{\xi} - \underline{x}, 23) + S_{-\infty}(\underline{x}, 12)] f^{(0)}(1)f^{(0)}(2)f^{(0)}(3) \end{aligned} \quad (26)$$

The corresponding one-particle equation, ignoring the transient of order of the collision time, is as follows:

$$\begin{aligned} \frac{\partial f^{(1)}}{\partial t_1} + \frac{\partial f^{(0)}}{\partial t_2} - \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial}{\partial \underline{v}_1} \int d\underline{\xi} d\underline{v}_3 S_{-\infty}(\underline{x}, 12) [f^{(1)} f^{(0)} + f^{(1)} f^{(0)}] \\ = \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial}{\partial \underline{v}_1} \int d\underline{\xi} d\underline{v}_3 [S_{-\infty}(\underline{x}, \underline{\xi}, 123) \\ - S_{-\infty}(\underline{x}, 12) S_{-\infty}(\underline{\xi}, 13) - S_{-\infty}(\underline{x}, 12) S_{-\infty}(\underline{\xi} - \underline{x}, 23) \\ + S_{-\infty}(\underline{x}, 12)] f^{(0)}(1)f^{(0)}(2)f^{(0)}(3) \end{aligned} \quad (27)$$

The variation of  $f^{(0)}$  on the  $t_2$  time scale can only be determined by the condition of non-secularity of  $f^{(1)}$  in the long time limit of  $t_1$ . In the limit of  $t_1 \rightarrow \infty$ , by the well known H-theorem of the Boltzmann (binary) collision integral,  $f^{(0)}$  goes to the Maxwellian distribution.

It is not difficult to show that the right hand side of Eq. (27) vanishes for  $f^{(0)}$  equal to the Maxwellian distribution. Therefore we have, by the condition of non-secularity, that

$$\frac{\partial f^{(0)}}{\partial t_2} = 0 \quad (28)$$

and

$$\begin{aligned} \frac{\partial f^{(1)}}{\partial t_1} = & \frac{n}{m} \left[ \frac{d\mathbf{x}}{dt} \frac{d\mathbf{v}_2}{dt} \frac{d\mathbf{f}}{d\mathbf{x}} \cdot \frac{\partial}{\partial \mathbf{v}_1} S_{-\infty}(\mathbf{12}) [f^{(1)}(\mathbf{1})f^{(0)}(\mathbf{2}) + f^{(1)}(\mathbf{2})f^{(0)}(\mathbf{1}) \right. \\ & + \frac{n}{m} \left[ \frac{d\mathbf{x}}{dt} \frac{d\mathbf{v}_2}{dt} \frac{d\mathbf{f}}{d\mathbf{x}} \cdot \frac{\partial}{\partial \mathbf{v}_1} \left[ \frac{d\mathbf{x}}{dt} \frac{d\mathbf{v}_3}{dt} [S_{-\infty}(\mathbf{x}, \mathbf{x}, \mathbf{123}) - S_{-\infty}(\mathbf{12})S_{-\infty}(\mathbf{x}, \mathbf{13}) \right. \right. \\ & \left. \left. - S_{-\infty}(\mathbf{12}) S_{-\infty}(\mathbf{x}, \mathbf{x}, \mathbf{23}) + S_{-\infty}(\mathbf{x}, \mathbf{12})] f^{(0)}(\mathbf{1})f^{(0)}(\mathbf{2})f^{(0)}(\mathbf{3}) \right] \quad (29) \end{aligned}$$

The second term on the right side of Eq. (29) is the triple collision integral which has been obtained by Choh and Uhlenbeck,<sup>5</sup> Green,<sup>6</sup> Rice, Kirkwood, and Harris,<sup>7</sup> and Resibois.<sup>8</sup> Equation (28) indicates a self-termination of the multiple-time-scale formulation, i.e., there is no variation after the time scale of kinetic evolution, which is what one would expect physically for a homogeneous system.

It is well known that on the binary collision level a system with any disturbance will go to the thermal equilibrium as indicated by the H-theorem of Boltzmann. It is of interest to see whether Eq. (29), together with Eq. (9), will force a system into thermal equilibrium, i.e., the one-particle function becomes the Maxwell-Boltzmann distribution up to the order of  $\epsilon$ . Since the expansion of the hierarchy in terms of  $\epsilon$  is viewed as an asymptotic series, it is only consistent to answer the

above question order by order. First, because of the H-theorem of the binary collision integral we know  $f^{(0)}$  becomes Maxwellian in thermal equilibrium. With  $f^{(0)} = f_{\max}$ , the triple collision integral vanishes and we are left with

$$\frac{\partial f^{(1)}}{\partial t_1} = \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial}{\partial \underline{v}_1} S_{-\infty}(12) [f^{(1)}(1)f^{(0)}(2) + f^{(1)}(2)f^{(0)}(1)] \quad (30)$$

Combining this with the lowest order approximation (Boltzmann's equation), we obtain

$$\frac{\partial}{\partial t_1} (f^{(0)} + \epsilon f^{(1)}) = \frac{n}{m} \int d\underline{x} d\underline{v}_2 \frac{d\phi}{d\underline{x}} \cdot \frac{\partial}{\partial \underline{v}_1} [f^{(0)}(1) + \epsilon f^{(1)}(1)] [f^{(0)}(2) + \epsilon f^{(1)}(2)] + O(\epsilon^2)$$

By the H-theorem for this collision integral, we know that  $f^{(0)} + \epsilon f^{(1)}$  goes to the Maxwellian distribution in thermal equilibrium. If we choose  $f^{(1)}(t_0=0) = 0$  initially,  $f^{(1)}$  goes to zero in thermal equilibrium because Eqs. (29) and (30) preserve the normalization of  $f^{(1)}$ . Such a statement apparently holds also for the higher order approximations.

#### IV. Discussion.

Using the multiple-time-scale method, it is found that the triple collision integral for a classical Boltzmann gas is identical to that obtained by Choh and Uhlenbeck. The functional dependence of the multiple particle functions on the one particle function is nevertheless found to be locally invalid for particles having large separations at time  $t_0$  and with their relative velocity oriented in such a way that they were in collision at  $t_0 = 0$ . Such locally non-functional behavior of the multiple particle functions is related to the inseparability of the time and length scales caused by the two successive binary collisions which happen at a time interval of the order of the mean free time. A new scaling for such a local region is given. The self-contained (or Markoffian) one-particle description of the system which is true outside such a region is found to be impossible. The hierarchy equations have to be solved simultaneously on the kinetic time scale (of the order of the mean free time). However, due to the very special nature of the relative velocity in this local breakdown, the contribution of this local region to the one-particle function comes into play only at orders higher than the triple collision level. Furthermore, if the pair potential is limited in its range, such a local contribution can be neglected even in higher orders.

REFERENCES

1. N. N. Bogoliubov, Problems of a Dynamical Theory in Statistical Physics (1947). See: Studies in Statistical Mechanics (Inter-Science Publishers, Inc., New York, 1962) Vol. 1.
2. I. Prigogine and P. Resibois, *Physica* 27, 629 (1961).
3. M. Green, National Bureau of Standards Rept. 3327 (1955).
4. Review article by S. Rice and H. Frisch, *Ann. Rev. Phys. Chem.* 11, 187 (1960); contains the work by Kirkwood and his co-workers.
5. S. T. Choh and G. E. Uhlenbeck, "The Kinetic Theory of Dense Gases," Univ. of Michigan report (1958).
6. M. Green, *Physica* 24, 393 (1958).
7. S. Rice, J. Kirkwood, and R. Harris, *Physica* 26, 717 (1961).
8. P. Resibois, *J. of Math. Phys.* 4, 166 (1963).
9. E. G. D. Cohen, *Physica* 27, 163 (1961).
10. E. G. D. Cohen, *Physica* 28, 1025 (1962).
11. G. Sandri, *Ann. Phys. (N.Y.)* 24, 332, 380 (1963).
12. J. E. McCune, G. Sandri, E. A. Frieman, Third Symposium Rarefied Gas Dynamics, Vol. 1 (Academic Press, New York, 1963).
13. C. H. Su, (Ph.D. thesis) "Kinetic Theory of a Weakly Coupled Gas," Princeton University (1964) (to be published).
14. E. G. D. Cohen, Fundamental Problems in Statistical Mechanics (North Holland, Amsterdam, 1962).

$$\lim_{t_0 \rightarrow \infty} \int_0^{t_0} d\tau \left[ S_{-t_0}(12) - S_{-\tau}(12) \right] f^{(0)}(1) f^{(0)}(2)$$

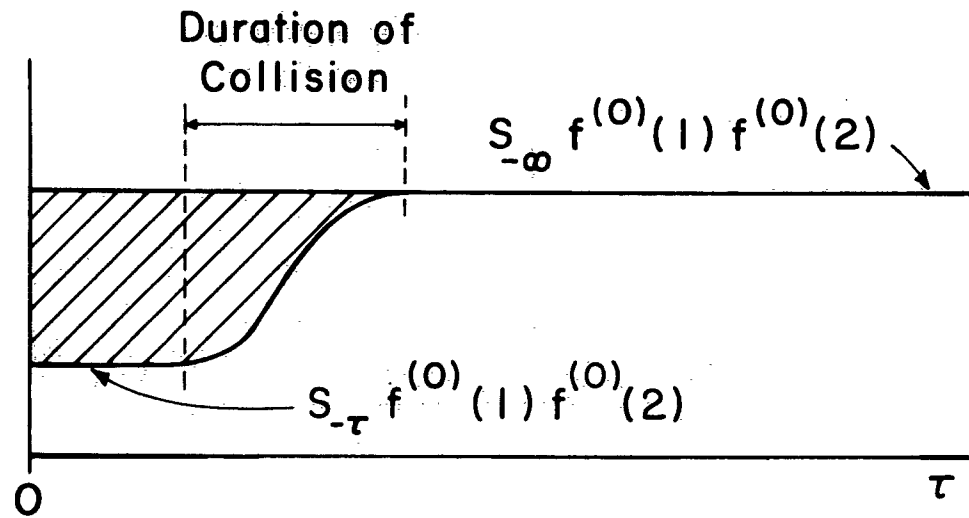


Fig. 1 a

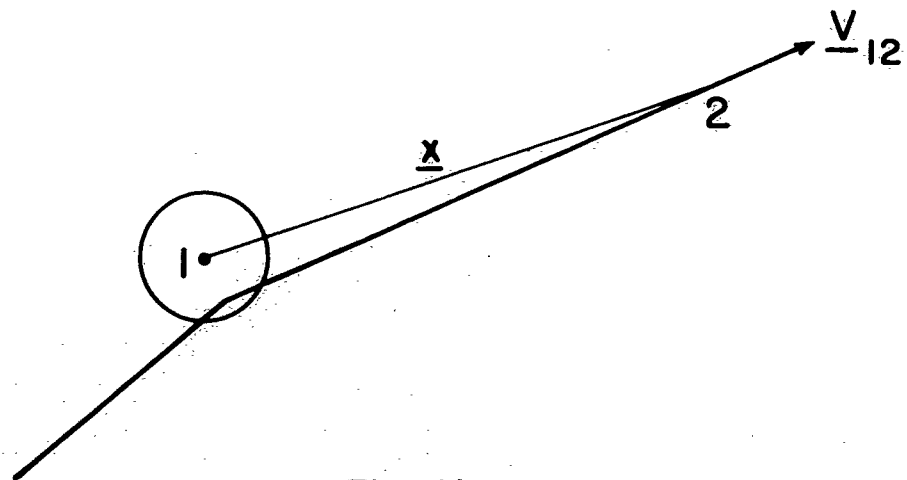


Fig. 1 b

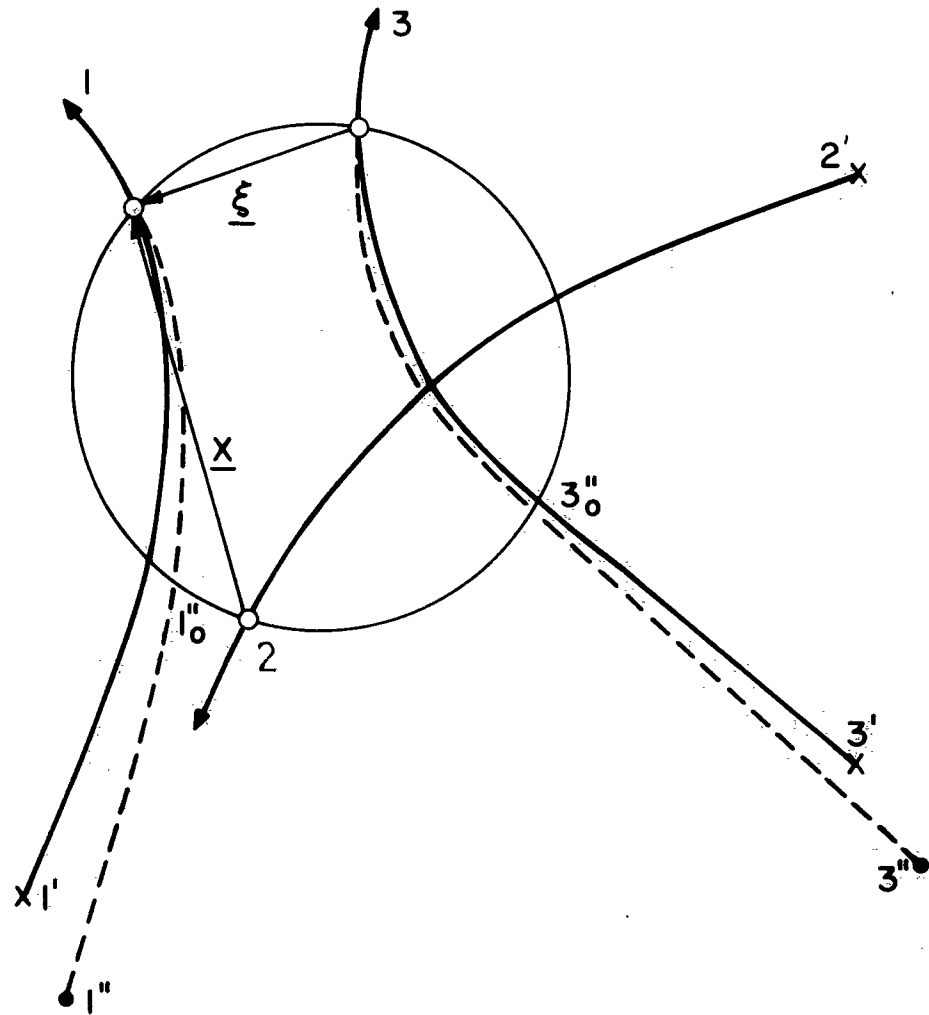


Fig. 2

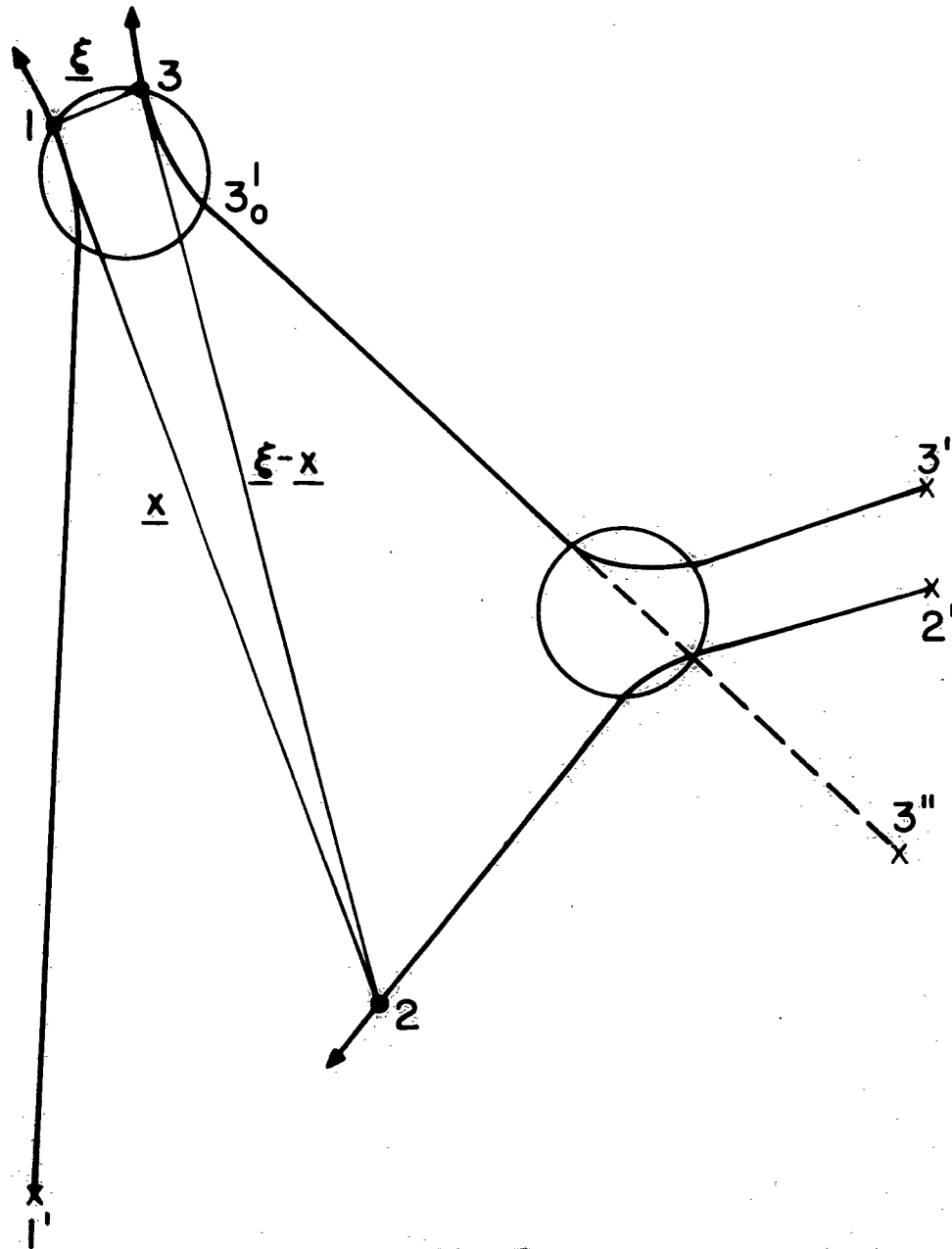


Fig. 3



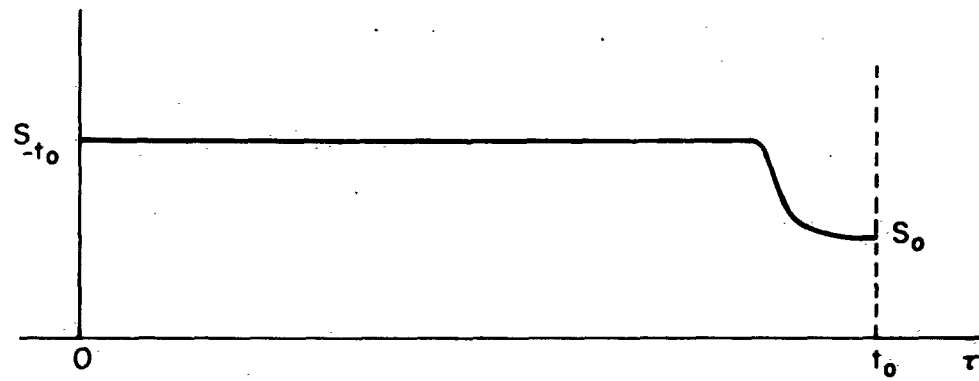


Fig. 4